Effects of γ-Ray Irradiation on Polymers. (I)

Effects of γ-Ray Irradiation on Elongated Filaments of Low and High Density Polyethylenes

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The effects of γ-ray irradiation in vacuum and in air on physical properties have been studied of the high and low density polyethylene filaments elongated to various degrees. The gel fraction of the vacuum-irradiated filaments increased with dose and was independent of the degree of elongation. The low density polyethylene irradiated in air was insoluble at 8.2×10^6 r and 1.5×10^7 r, whereas at a higher dose it was soluble in xylene of 80°C except the samples of the low degree of elongation. The high density polyethylene irradiated in air dissolved in xylene of 120°C for all radiation doses used. Using a theory proposed by Charlesby regarding the relation between solubility and dose, our experimental curve was found to be in an approximate agreement with the theoretical curve of $f=0.5$. G-values of crosslinking at the gelation point was 4.2 for the low density polyethylene and 4.9 for the high density polyethylene. The density of these filaments increased slightly with dose in vacuum-irradiation, and remarkably in air.

INTRODUCTION

The changes of the physical and chemical properties of polyethylene by crosslinking and degradation reactions, which occur under high energy irradiation, are well-known. It is interesting to study the effects of the molecular structure, the degrees of crystallinity and of orientation on these changes of the materials by irradiation.

In this paper, the effects of dose, gel fraction, degree of swelling and density on the properties will be studied with the use of elongated filaments of low and high density polyethylene.

MATERIALS

Two types of polyethylene filaments were used : (1) low density branched polyethylene containing vinylidene-unsaturation and of low crystallinity, (2) Ziegler type linear polyethylene containing vinyl-vinylene-vinyliden-unsaturations and of high crystallinity. These filaments were put at our disposal by the courtesy of the Toyo Rayon Co. Ltd. The filaments were spun at a rate of 7 m/min. and elongated at 80°C. for low density polyethylene and at 95°C. for high density polyethylene.

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Table 1. Denier of filaments.

	Low density polyethylene				High density polyethylene			
Sample	L-1	L-3	L-4	L-5	H-1	H-3	H-5	H-6
Degree of elongation	1	2.4	3.2	5.8	1	3.0	4.6	5.6
Denier	1203	513	378	207	1329	438	288	238

Table 2. Degree of crystallinity and density of filaments.

	Low density polyethylene					High density polyethylene				
Degree of elongation	1	3.3	4.6	6.0	8.0	1	3.1	5.1	5.7	6.8
Degree of crystallinity %	48	50	54	55	60	63	66	69	70	72
Density	0.9098	.9142	.9155	.9178	.9215	0.9361	.9382	.9405	.9408	.9419

The denier of these filaments is shown in Table 1. Number-average molecular weight of low density polyethylene determined by the viscosity measurement was 2.1×10^4 and that of high density one 9.6×10^4. According to our results reported previously[1], the crystallinity and the density of these samples are summarized in Table 2.

IRRADIATION

γ-ray-irradiations were performed both in vacuum and in air, using a cobalt-60 source of 200 curies at the Institute for Chemical Research, Kyoto University. In vacuum-irradiation, the sample was irradiated in a sealed glass tube degassed into 10^{-3} mm. Hg. The radiation data, radiation dose, rate and time of exposure are given in Table 3. In this Table, V and O represent the data obtained in vacuum and in air respectively.

Table 3. Radiation data.

Run No.	Dose rate r/hr.	Exposure time hr.	Dose Mr.
V-1 O-1	1.4×10^4	151	2.4
V-2 O-2	7.0×10^4	116-27′	8.2
V-3 O-3	〃	209-32′	15
V-4 O-4	〃	510-34′	35
V-5 O-5	3.1×10^4	320-00′	99

RESULTS AND DISCUSSION

(1) Degree of Swelling and Solubility

For the purpose of studying the variation of the degree of crosslinking by irradiation, swelling and solubility of the irradiated samples were measured.

As a solvent, xylene of 80°C. for low density polyethylene and of 120°C. for high density polyethylene were employed. The sample was dried at 80°C. and weighed after the measurements, from which the relation between radiation dose and fraction of gel of irradiated samples was estimated. The results are shown in Tables 4 and 5.

Table 4. Dose and fraction of gel.

Sample	Unirradiated	Vacuum-irradiation Dose×10⁻⁶r					Air-irradiation Dose×10⁻⁶r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
L-1	Sol.	35.4	52.9 (47.0)	64.0 (59.8)	79.8	93.4	Sol.	33.2	37.9	17.0	Sol.
L-3	〃	32.4	53.9	66.8	75.3	93.3	〃	38.0	32.5	8.8	〃
L-4	〃	36.8	52.0 (41.0)	65.4 (60.5)	80.3	91.0	〃	—	24.5	Sol.	〃
L-5	〃	28.1	53.0	61.1	79.2	88.2	〃	—	25.0	〃	〃
H-1	Sol.	Sol.	10.6	41.7	72.4	85.8	Sol.	Sol.	Sol.	Sol.	7.1
H-3	〃	〃	9.4	40.5	63.5	86.4	〃	〃	〃	〃	Sol.
H-4	〃	〃	—	40.7	68.3	86.9	〃	〃	〃	〃	〃
H-5	〃	〃	10.4	36.9	76.8	85.6	〃	〃	〃	〃	〃

Table 5. Changes in degree of swelling of gel with dose.

Sample	Unirradiated	Vacuum-irradiation Dose×10⁻⁶r					Air-irradiation Dose×10⁻⁶r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
L-1	Sol.	83	27	20	12	10	Sol.	108	78	115	Sol.
L-3	〃	117	30	18	20	11	〃	125	115	300	〃
L-4	〃	79	29	21	16	10	〃	—	133	Sol.	〃
L-5	〃	132	35	26	19	14	〃	—	153	〃	〃
H-1	Sol.	Sol.	80	38	13	9	Sol.	Sol.	Sol.	Sol.	47
H-3	〃	〃	—	40	20	8	〃	〃	〃	〃	Sol.
H-5	〃	〃	—	39	17	10	〃	〃	〃	〃	〃
H-6	〃	〃	—	49	16	9	〃	〃	〃	〃	〃

The solubility of the vacuum-irradiated samples decreased upon increasing the radiation dose. When the samples were irradiated in air, the solubility decreased with increasing radiation dose up to 1.5×10^7 R, and at still higher doses increased through a minimum. The highly elongated samples dissolved completely at higher doses. The solubility of polymer having crosslinkage depends on the density of the crosslinking, molecular weight and molecular weight distribution. The relation between solubility s and crosslinking index γ for the the uniform distribution derived by Flory[2] may be shown as follows.

$$s = e^{-\gamma(1-s)}$$

Charlesby gave the following equation for the Poisson distribution.

$$s = (1+\gamma-\gamma s)^2 - 1$$

Futhermore, Charlesby[3] derived an equation for the case when the crosslinking and the fracture of main-chain occur simultaneously. He defined a new crosslinking index γ' as:

$$\gamma' = \frac{\gamma}{1+f\gamma},$$

where γ' is the number of crosslinked units per instantaneous primary weight-average molecule as opposed to the original primary number-average molecule to which γ refers, and f is a fraction of degradation to crosslinking. The observed solubility is plotted against the radiation dose with Charlesby's theoretical curve in Figs. 1 and 2. For vacuum-irradiation, the observed solubility is in a rough agreement with a theoretical value of $f=0.5$. Charlesby[4] reported that f was equal to 0.3-0.4 for pile irradiated low density polyethylene. The solubility of the vacuum-irradiated polyethylene was independent of the degree of elongation but this was not the case in air-irradiation. It is doubtful whether the solubility data can be interpreted in terms of the degree of elongation only or not, when the samples were irradiated in air, since the sample highly elongated had a larger surface area[5].

The G-value of crosslinking at the gelation point was determined using the equation.

$$G_{el} = \frac{\gamma \times 6.02\times10^{23}\times100}{2\times r\times5.8\times10^{13}\times M_n}$$

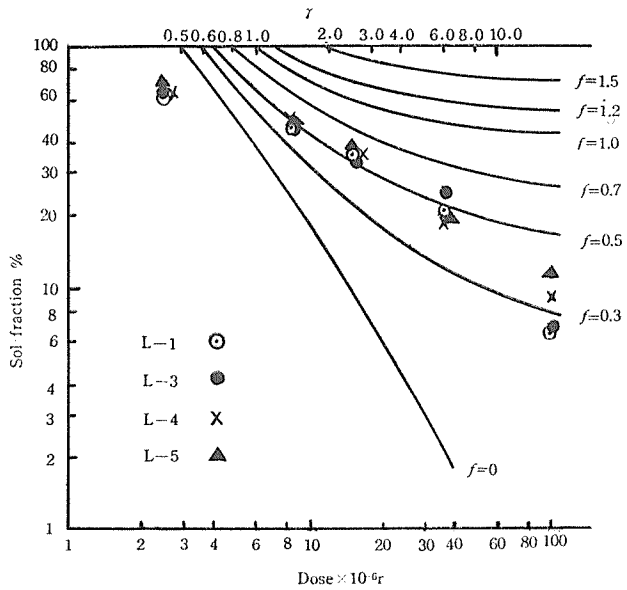

Fig. 1. Solubility-dose curves of the vacuum-irradiated low density polyethylene.

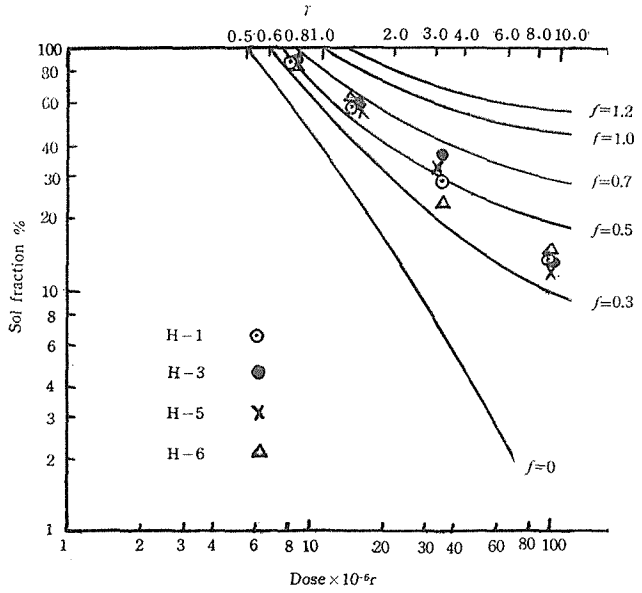

Fig. 2. Solubility-dose curves of the vacuum-irradiated high density polyethylene.

where r is the radiation dose and M_n the number-average molecular weight. The G-value of crosslinking determined by these observation was 4.2 for the low density polyethylen and 4.6 for the high density polyethylen. These values are in an approximate agreement with the G-values reported by Charlesby[4] and Kawai and others[7]. The difference between the G-values of low and high density polyethylenes could not be found[8], as Epstein[9] and Waddington[10] reported. Molecular weight per crosslinked unit, $\overline{M}_c$, could be determined from the swelling data with the use of the following equations[11,12].

$$Q=1+\frac{\rho_1}{\rho_0}\frac{\overline{W}_s}{\overline{W}_1}-\frac{\rho_1}{\rho_0}=\frac{1}{v_2},$$

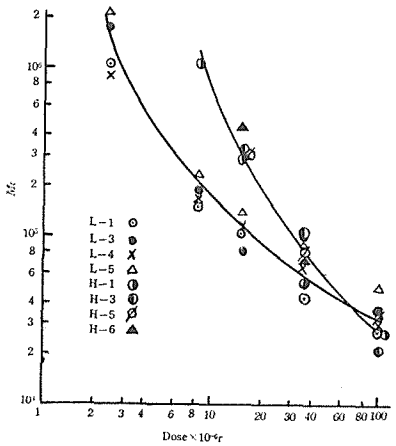

Fig. 3. $\overline{M}c$ as a function of dose of the vacuum-irradiated filaments.

$$\overline{M_c} = \rho_1 V_0 \left(v_2^{1/2} - \frac{v_2}{2} \right) \Big/ \left(\frac{1}{2} - \mu \right) v_2^2 ,$$

where Q, v_2, ρ_1, ρ_2 and V_0 are the swelling ratio by volume, the volume fraction of polymers in swollen network, the densities of solvent and gel fraction, and the volume of the undeformed polymer-network respectively.

Furthermore, concentration of crosslinking per gram, c and G-value of crosslinking at any dose were estimated from $\overline{M_c}$. These results determined with g taken as unity and M_{ng} as M_n are given in Table 6 and Fig. 3.

Though the moleccular weight of high density polyethylene was lerger than that of low density polyethylene, as described above, $\overline{M_c}$ of the former was

Table 6. Changes of v_2, $\overline{M_c}$, C, G_{cl} from swelling data by the irradiation.

Sample	Unir-radiated	Vacuum-irradiation Dose×10⁻⁶ r					Air-irradiation Dose×10⁻⁶ r				
		2.4	8.2	15	35	99	2.4	8.2	15	35	99
v_2											
L-1	Sol.	0.012	0.036	0.049	0.080	0.101	Sol.	0.009	0.012	0.008	Sol.
L-3	〃	0.008	0.033	0.054	0.049	0.088	〃	0.008	0.009	0.003	〃
L-4	〃	0.012	0.034	0.047	0.061	0.097	〃	—	0.007	Sol.	〃
L-5	〃	0.007	0.028	0.038	0.051	0.072	〃	—	0.006	〃	〃
H-1	Sol.	Sol.	0.012	0.025	0.073	0.106	Sol.	Sol.	Sol.	Sol.	0.020
H-3	〃	〃	—	0.024	0.047	0.125	〃	〃	〃	〃	Sol.
H-5	〃	〃	—	0.024	0.056	0.094	〃	〃	〃	〃	〃
H-6	〃	〃	—	0.019	0.059	0.111	〃	〃	〃	〃	〃
$\overline{M_c}\times10^{-4}$											
L-1	Sol.	103	15.7	10.3	4.22	2.87	Sol.	157	93	174	Sol.
L-3	〃	179	18.7	8.02	10.3	3.62	〃	200	174	859	〃
L-4	〃	93	17.7	10.4	6.69	3.06	〃	—	222	Sol.	〃
L-5	〃	220	24.2	14.8	8.82	5.02	〃	—	281	〃	〃
H-1	Sol.	Sol.	105	30.3	5.15	2.74	Sol.	Sol.	Sol.	Sol.	42.0
H-3	〃	〃	—	33.3	10.4	2.08	〃	〃	〃	〃	Sol.
H-5	〃	〃	—	31.7	7.99	3.33	〃	〃	〃	〃	〃
H-6	〃	〃	—	46.1	7.20	2.53	〃	〃	〃	〃	〃
$C\times10^{-5}$ mol.											
L-1	Sol.	4.81	5.08	5.24	5.95	6.50	Sol.	4.79	4.81	5.05	Sol.
L-3	〃	4.79	5.03	5.38	5.24	6.14	〃	4.78	4.79	4.82	〃
L-4	〃	4.81	5.04	5.24	5.51	6.39	〃	—	4.78	Sol.	〃
L-5	〃	4.78	4.97	5.10	5.32	5.66	〃	—	4.78	〃	〃
H-1	Sol.	Sol.	1.09	1.21	2.01	2.87	Sol.	Sol.	Sol.	Sol.	1.16
H-3	〃	〃	—	1.19	1.53	3.44	〃	〃	〃	〃	Sol.
H-5	〃	〃	—	1.20	1.67	2.54	〃	〃	〃	〃	〃
H-6	〃	〃	—	1.15	1.73	3.01	〃	〃	〃	〃	〃

G-value of crosslinking from swelling data.

L-1	Sol.	20.8	6.4	3.6	1.7	0.7	Sol.	6.0	3.3	1.5	Sol.
L-3	〃	20.7	6.4	3.7	1.6	0.7	〃	6.1	3.3	1.4	〃
L-4	〃	20.8	6.4	3.6	1.6	0.7	〃	—	3.3	Sol.	〃
L-5	〃	20.7	6.3	3.5	1.6	0.6	〃	—	3.3	〃	〃
H-1	Sol.	Sol.	13.8	8.4	5.9	3.0	Sol.	Sol.	Sol.	Sol.	12.2
H-3	〃	〃	—	8.2	4.5	3.6	〃	〃	〃	〃	Sol.
H-5	〃	〃	—	8.3	4.9	2.6	〃	〃	〃	〃	〃
H-6	〃	〃	—	7.9	5.1	3.0	〃	〃	〃	〃	〃

larger than that of the latter at small radiation doses.

And at higher doses, $\overline{M_c}$'s of two types of polyethylenes become nearly equal. The G-values of crosslinking determined from the swelling data decreased with dose, in accordance with the result reported by Lawton[13] and Kawai[6,12]. Such a tendency may be attributed to our choice of M_n instead of M_{ng}. The value of crosslinking at higher radiation doses seems to be reliable, because M_{ng} can be supposed to be approximately equal to M_n in this case.

(2) Density

The density of these polyethylene filaments irradiated in vacuum and in air was measured by the floatation method in water-ethylalcohol solution at 25°C[14]. The variation of the density as a function of radiation dose is shown in Figs. 4 and 5.

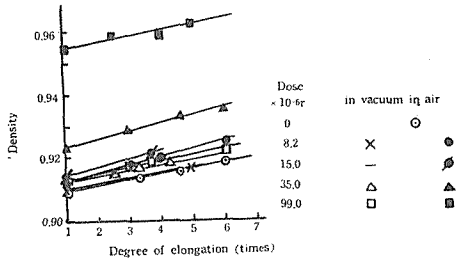

Fig. 4. Density as a function of degree of elongation of irradiated low density polyethylene.

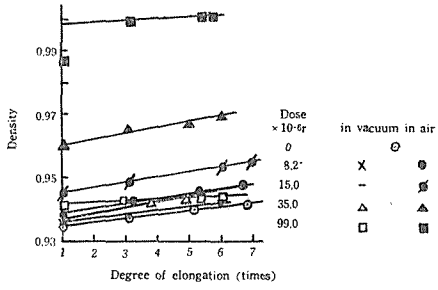

Fig. 5. Density as a function of degree of elongation of irradiated high density polyethylene.

The density of vacuum-irradiated polyethylene hardly increased with dose whereas that of air-irradiated remarkably increased. These results are similar to those of Woodward[15]. It was newly found that the long period of the crystalline part of the vacuum-irradiated samples hardly varied but the intensity increased with dose up to 1.5×10^7 r and decreased again at still higher doses. The considerable variation in the density of these filaments irradiated in air appears to be ascribed to the main-chain scission and oxidation.

(3) Effects of Atomosphere

The crosslinking occured more efficiently when the irradiation was perform-

ed in vacuum. This may be interpreted as an evidence that oxygen reacts on free radicals very easily[16,17].

(4) Effect of Orientation

The variations in crosslinking and density of the vacuum-irradiated polyethylene as a function of radiation dose were known to be independent of the degree of elongation. Considering the difference in thickness of the filaments[5], it is not clear whether the degree of elongation is an only factor in terms of which the solubility and density data of the air-irradiated samples at high doses can be interpreted.

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